(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 048 083 A1

EUROPEAN PATENT APPLICATION

(12)

(21) Application number: 81303264.6

(22) Date of filing: 16.07.81

(51) Int. Cl.³: C 23 C 7/00
C 23 C 3/00, C 23 C 9/00
C 23 C 17/00, B 05 D 1/00
B 05 D 1/08

(30) Priority: 17.09.80 JP 128738/80

(43) Date of publication of application:
24.03.82 Bulletin 82/12

(84) Designated Contracting States:
DE FR GB IT

(71) Applicant: MITSUBISHI JUKOGYO KABUSHIKI KAISHA
5-1, Marunouchi 2-chome Chiyoda-ku
Tokyo(JP)

(72) Inventor: Harada, Yoshio Takasago Technical Institute
Mitsubishi Jukogyo Kabushiki Kaisha 1-1, Shinhama
2-chome, Arai-cho Takasago-shi Hyogo-ken(JP)

(72) Inventor: Nakamori, Masaharu Takasago Tech. Institute
Mitsubishi Jukogyo Kabushiki Kaisha 1-1, Shinhama
2-chome, Arai-cho Takasago-shi Hyogo-ken(JP)

(72) Inventor: Saika, Keigo Takasago Technical Institute
Mitsubishi Jukogyo Kabushiki Kaisha 1-1, Shinhama
2-chome, Arai-cho Takasago-shi Hyogo-ken(JP)

(72) Inventor: Fukue, Ichiro Takasago Technical Institute
Mitsubishi Jukogyo Kabushiki Kaisha 1-1, Shinhama
2-chome, Arai-cho Takasago-shi Hyogo-ken(JP)

(72) Inventor: Takaoka, Shigefumi Takasago Tech. Institute
Mitsubishi Jukogyo Kabushiki Kaisha 1-1, Shinhama
2-chome, Arai-cho Takasago-shi Hyogo-ken(JP)

(72) Inventor: Maekawa, Atsushi Takasago Techn. Institute
Mitsubishi Jukogyo Kabushiki Kaisha 1-1, Shinhama
2-chome, Arai-cho Takasago-shi Hyogo-ken(JP)

(74) Representative: Rushton, Ronald et al,
SOMMERVILLE & RUSHTON 89 St. Peters Street
St. Albans Herts AL1 3EN(GB)

(54) Surface treatment method of heat-resistant alloy.

(57) A method of surface treatment of a member made of heat-resistant alloy comprises spraying onto the surface of said member as a first layer a coating of a heat resistant material comprising for example a metal such as Ni or Cr or a Ni-Cr alloy or a compound thereof. A liquid coating containing a corrosion resistant material is then applied as a second layer on to the first layer. The member is then heat treated to effect penetration by diffusion of one coating into the other.

EP 0 048 083 A1

"Surface Treatment Method of Heat-Resistant Alloy"

This invention relates to a method of surface treatment of a member of heat-resistant alloy for use in turbines, blowers, boilers or the like to render it resistant to high temperature oxidation as well as to high temperature corrosion.

In industrial gas turbines using petroleum or natural gas as the fuel, gas temperature at the turbine inlet tends to become higher as the turbine efficiency is improved. On the other hand, as the available fuel supply has changed for the worse in recent years, the fuels used for the turbines have been diversified and the content of corrosive impurities in the fuels such as sulphur (S), sodium (Na), vanadium (V), and so forth has tended to increase. As a result, so-called "hot parts" such as the blades and burners of turbines, that are exposed to these high temperature gases, are subjected to extremely severe high temperature oxidation as well as high temperature corrosion.

These hot parts have conventionally been made primarily of heat-resistant alloys. In particular turbine blades consist of Ni- and Co-based alloys called "ultra-alloys". However, since high temperature strength is generally a top

priority requirement for these ultra-alloys, they have the drawback that their corrosion resistance and oxidation resistance are not satisfactory. Various attempts have therefore been made to provide these heat-resistant alloys with oxidation resistance and corrosion resistance and various surface treatment methods using for example chemical and physical techniques have been employed. However, none of these methods has been really satisfactory as regards efficiency and cost.

The present invention is directed to providing a method which overcomes the deficiences of the previous methods. Accordingly, in order to provide a member of heat-resistant alloy with high temperature oxidation resistance and high temperature corrosion resistance, the present invention provides a surface treatment method which is characterized by the steps of coating by spraying onto the surface of said member in the form of a substrate, a heat-resistant material of metals such as Ni and Cr or Ni-Cr alloys or their compounds as a first layer, then applying, as a second layer, a liquid coating containing metals such as Aℓ, Si, Vr, Ts and the like or their alloys or compounds as the corrosion-resistant material by means of spray-coating, brush-coating or the like, and heat-treating the coated surface.

The surface treatment method of the present invention provides the characterizing features as illustrated in Table 1 in comparison with the conventional methods.

Table 1

		Method of this Invention	Conventional Methods				
	Method	Spraying & Slurry coating & diffusion penetration	Slurry coating & diffusion penetration	CVD* & diffusion penetration	plasma spraying	Low pressure plasma spraying	electron beam vacuum deposition
	Metals	CrNi CrNiAl CrNiAlSi others	Cr Al Al-Si others	Cr Al Al-Si	NiCrSi NiCrAlSiY ZrO_2 MgO	NiCrAlY CoCrAlSiY others	NiCrAlY CoCrAlY others
Features of method	Productivity	medium	great	great	medium	small	small
	cast	medium	small	small	medium	great	extremely great
	Utilizability	done	done	done	partly done	partly done in U.S.	partly done in U.S.
Properties of coating	adhesion	good	fair	good	fair	good	good
	corrosion resistance	good	good in low temp range, bad in high temp range	good in low temp range, bad in high temp range	considerably bad	good	good
	uniformity	good	good	good	fair	fair	good
	surface coarseness	good	good	bad	bad	fair	good
	Overall evaluation	excellent	good	good	fair	good	good

* CVD : Chemical vapor deposition

The present invention will be now described in more detail by reference to an example in accordance therewith.

A substrate of Udimet 520 (by weight 19% Cr, 12% Co, 6% Mo, 3% Ti, 2% Aℓ, 1% Fe, Ni-Bal), widely used as an ultra-alloy for the hot parts of a gas turbine, was treated in the following sequence:

(1) After the surface of the substrate had been cleaned with an alkaline emulsion cleaning agent, steam cleaning was carried out using a Fluron type solvent. The surface was further blasted using an $A\ell_2O_3$ blast.

(2) A Ni-Cr (50/50 by weight) alloy was applied as a coating to form a first layer having a thickness of about 50μ by plasma spraying.

(3) The surface of the sprayed-on first layer was blasted using $A\ell_2O_3$ to remove any oxide film formed on its outermost surface.

(4) The surface of the sprayed-on first layer was coated by spraying on a coating slurry formed by dispersing Aℓ and SiO_2, each having a particle size of about 0.1 to 1μ, in an organic carrier (alcohol, solvent naphtha, etc) to form a second layer.

(5) After these treatments, the substrate was placed in an electric furnace and was held at 80^{0}C. (± 5^{o}C) for

20 minutes to evaporate and remove the liquid. After being further held at 330°C (± 5°C) for 15 minutes, the substrate was withdrawn from the furnace.

(6) The substrate was held at 1,080°C for 4 hours inside a hydrogen furnace, was cooled in the furnace and was then withdrawn.

Above mentioned step (4) could be carried out using a mixture of fine Aℓ particles with $A\ell_2O_3$ powder in a mixing ratio by weight of 80/20 or 50/50 or a mixture of Aℓ with SiO_2 in a mixing ratio by weight of 80/20 or 50/50. Also step (6) could be carried out using a vacuum furnace in place of the hydrogen furnace.

Although in this example Udimet 520 has been treated by the method of the invention by way of example, similar excellent results can also be obtained when treating the surfaces of other substrates such Ni-based alloy, Co-based alloy and stainless steel.

The coated surface of the substrate provided by the above described method had an extremely smooth and flat surface and Aℓ and Si from the second layer sufficiently penetrated by diffusion into the first layer, thereby completely eliminating the fine pores of the first layer. Hence, the composite coating was rendered wholly homogeneous.

In other words, since the melting point of Al is 660°C., Al was fused due to the heat-treatment and penetrated into the fine pores, thus presumably rendering the surface smooth and flat. Further, it was confirmed that a part of Al and Si reached and was diffused also into the substrate.

Table 2 illustrates the results of fly-ash errosion resistance test, corrosion resistance test, and practical application test using gas turbine blades, each test being applied to a member treated by a method in accordance with the present invention and a member treated by a conventional method. The composite coating produced by the method in accordance with the present invention had a better performance in comparison with that produced by the conventional method in the fly-ash errosion resistance test and the corrosion resistance test. In the practical application test using gas turbine blades, too, the coated blade produced using the method of the present invention exhibited the tendency that the deposition amount of the fuel ash became smaller. In a thermal inpact test comprising holding the testpiece at 1,100°C. for 15 minutes, then charging it into the water at 20°C. and repeating these procedures five times, the composite coating produced by the method of the present invention did not suffer peeling or cracking and had extremely good adhesion.

Table 2

	Conventional method		Method of this Invention
	Ni-Cr spraying (about 50μ)	diffusion penetration (CVD*) (about 50μ)	Ni-Cr spraying + slurry coating (40μ + 30μ)
Fly-ash errosion resistance test (fly-ash particle size 16μ fly-ash concentration $5g/m^2$) gas flow velocity 10m/min. No. of revolution of T/P 3,900 r.p.m.	° Tends to be damaged in about 5 hrs. ° 50% of sprayed layer off in about 10 hrs. ° Sprayed layer disappears in about 20 hrs.	° No abnormality in about 5 hrs. ° Tends to be damaged in about 10 hrs. ° 1/2 of coating falls off in about 20 hrs. ° Penetration portion disappears in about 50 hrs.	° Tends to be damaged in about 10 hrs. ° 1/2 of coating fall off in about 50 hrs. ° Considerable portion of coating still remains after about 100 hrs.
Corrosion resistance test (V_2O_5-Na_2SO_4 coating, similated combustion gas) flow; 900°C, 10 hrs.	A part of sprayed layer falls off and penetration of V_2O_5-Na_2SO_4 component to boundary of substrate is observed.	Overall corrosion occurs and partly proceeds to boundary of substrate.	Slight overall corrosion occurs on the surface layer portion but no abnormality occurs inside the coating.
Practical application test using gas turbine blade (Gas temp ..1,000°C Metal temp .. 800°C) 200 hrs.	° Deposition of combustion ash is great. ° 70% to 80% of sprayed layer falls off.	° Deposition of combustion ash is great. ° Thickness of coating decreases to about 1/2 of initial thickness.	° Deposition of combustion ash is great. ° Slight overall corrosion occurs but most coating remains.

* CVD : Chemical vapor deposition

Claims.

1. A method of surface treatment of a member made of heat-resistant alloy characterised by the steps of spraying onto the surface of said member a coating of a heat-resistant material, applying a liquid coating containing a corrosion-resistant material onto the sprayed-on coating and then heat treating said member to effect penetration by diffusion of one coating into the other.

2. A method according to claim 1, characterised in that said sprayed-on coating comprises Ni or Cr or a Ni-Cr alloy or a compound of Ni and/or Cr.

3. A method according to Claim 1 or Claim 2, characterised in that said liquid coating comprises a slurry.

4. A method according to any preceding claim, characterised in that said liquid coating contains at least one of the following, Aℓ, Si, Vr, Ts, or an alloy thereof or a compound thereof.

5. A method according to Claim 4, characterised in that the liquid coating comprises a slurry formed by dispersing Aℓ and SiO_2 in a liquid carrier.

6. A method according to Claim 5, characterised in that said Aℓ and SiO_2 have a particle size of about 0.1μ to 1μ.

7. A method according to Claim 4, characterised in that the liquid coating comprises a slurry formed by dispersing Al and Al_2O_3 in a liquid carrier.

8. A method according to any preceding claim, characterised in that the heat treatment includes the step of holding the member at about 1080°C for several hours.

9. A method according to Claim 8, wherein said step in the heat treatment is preceded by a heating step to evaporate the liquid, followed by a relatively short heat treatment at about 330°C.

10. A method of surface treatment of a member made of heat resistant alloy, substantially as hereinbefore described by way of example.

European Patent Office

EUROPEAN SEARCH REPORT

0048083
Application number

EP 81303264.6

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	GB - A - 2 009 251 (ROLLS-ROYCE LIMITED) * Abstract; claims; especially claims 3,6,7, 9,13-16 * --	1-8
	GB - A - 1 439 947 (UNION CARBIDE CORPORATION) * Pages 5-10 * --	1,2,5, 7
	US - A - 3 989 863 (R.P. JACKSON et al.) * Abstract; claims * --	1-5
	US - A - 3 837 894 (R.C. TUCKER, JR.) * Columns 7-14 * ----	1-5,7

CLASSIFICATION OF THE APPLICATION (Int. Cl.³)

C 23 C 7/00
C 23 C 3/00
C 23 C 9/00
C 23 C 17/00
B 05 D 1/00
B 05 D 1/08

TECHNICAL FIELDS SEARCHED (Int. Cl.³)

C 23 C
B 05 D

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	30-11-1981	SLAMA

EPO Form 1503.1 06.78